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PROCEEDINGS OF THE THIRD DAY.

WEDNESDAY, NOVEMBER 26, 1884.

The President, Dr. Brown, in the chair. The following papers were then read.

REPORT OF THE COMMISSION ON CHEMISTRY UPON THE YEAR'S PROGRESS.

I. ORGANIC AND PHYSIOLOGICAL CHEMISTRY.—BY PROF. E. H. S. BAILEY, *State University.*

In organic chemistry the field is a broad one, and it is only necessary to call attention to a few of the many discoveries of the year. Among these we note that M. A. Pohl has discovered a new putrefaction alkaloid from decayed flesh, having the composition $C_5H_{11}N$. G. Johnson recommends picric acid as a test for albumen in urine. A coagulum is formed when it is present. Use the solid or a saturated solution. This test is said to be more delicate than HNO_3. In the presence of KHO the solution changes from a deep yellow to a red. It is advisable to use equal volumes in all cases. The latest authorities on boric acid and borax as food preservatives, claim its use to be rather questionable. Their tendency is to decrease the amount of bile and of albuminous matter secreted. Hydric peroxide is coming into use as a disinfectant. A 3 per cent. solution in water is now made on a commercial scale. Hydric peroxide is very useful as an oxidizing agent in the place of nitric acid or bromine. It is particularly useful in the quantitative determination of sulphides and sulphites. Steps toward the artificial production of sinapic acid have been made by Remsen and Cole: the process is not yet completed. V. Meyer has shown that benzine obtained from coal tar, and that from benzoic acid, have different properties. From coal tar benzine a compound called theophane, containing sulphur, can be made, while this cannot be made from the other variety. Ethyl orange is one of the very best test solutions to distinguish between an acid and an alkali. From an alkali to an acid the change of color is from orange to rose. Nicol has brought forward a new hypothesis in regard to solution. He assumes that the solution of a salt in water is in consequence of the attraction of the molecule of water for a molecule of the salt exceeding that of the molecules of the salt for each other. At saturation the attraction of dissimilar molecules is counterbalanced by that of similar molecules.

From elaborate investigations, Fleischer has ascertained that sulphuric acid is a much better drying substance to use in a desiccator than calcic chloride. Solomon has made an investigation on the action of acids on starch. Musculus thought that by diastase, as well as by sulphuric acid, starch split up into one molecule of dextrine and one of sugar, and afterwards the acid slowly acted on the dextrine. Payen opposed this view, and showed that no such breaking up of the molecule took place, but that there was a gradual change. Opinions have been divided on the question, but Solomon shows that the change by acids is more rapid as the acid is stronger; it is in proportion to the time of action, but slower towards the end. Oxalic acid changes starch readily to sugar in three hours. The starch group is composed of x molecules of $C_6\ H_{10}\ O_5$, and is changed by the action into a simpler soluble starch, and this latter to dextrine. This final change is rapid. Sulphuric acid unites with a certain quantity of the dextrine and hydrates it, to give it up again to unite with a new quantity of dextrine, and change the latter to sugar. Recent patents have been taken out, by which an excellent quality of crystalized grape sugar can be made. The product is actually the hydrate, and does not absorb water readily. The chief modification from the ordinary method of manufacture is that the liquid grape sugar is absorbed by some porous substance. Experiments with a great variety of antiseptics, have shown that borax and boracic acid have the greatest power in this direction. The difference between new and stale bread is not on account of less water in the latter, but because a molecular change has taken place. The sticky or elastic condition of new bread is the only reason why it is less digestible than the stale. Recent French chemists claim to have discovered that alcohol is made in the system, even if sugar and other fermentable substances do not form part of the diet. Salicylic acid, if introduced into the system, is eliminated by the kidneys and liver. It usually does no harm, but as in certain conditions of the system, and in certain temperaments, it may do harm, its use as a food preservative cannot be recommended. Boiling oxygen has been used as a refrigerant. By its use, nitrogen may be obtained in snow-like flakes.

O'Shea has investigated bleaching powder, and finds the symbols to be $Ca—O—O\,Cl$. Water decomposes it into $Ca\,(O\,Cl_2)$ and $Ca\,Cl_2$. The specific gravity of liquid oxygen at minus 130° Centigrade is .899. Brucine is proposed as a test for tin. A nitric acid solution is used; this is diluted with water, and heated to boiling. It gives a purple color with stannous compounds.

II. AGRICULTURAL AND ANALYTICAL CHEMISTRY.— BY J. T. WILLARD, *State Agricultural College.*

In preparing this review of the Progress in Agricultural and Analytical Chemistry, the writer has been impressed by the mass of really valuable acquisitions of the past year. His only difficulty has been to select from this abundance that which is of the most importance and will most truly show the advances that have been made. This selection has doubtless been influenced somewhat by his personal appreciation of certain points, while another would have laid the greater stress upon other lines of work. Some very valuable papers from their length can only be referred to, while many of scarcely less value than those to be noticed presently cannot be alluded to at all.

A large portion of the work in agricultural chemistry has consisted of experiments to determine the effect of certain fertilizers on various crops. These experiments, while quite valuable, cannot be mentioned in detail. Prof. Paul Wagner has conducted a series of manuring experiments with such care that his results are almost as accordant as accurate chemical analyses. After five years' experience, he insists that a tolerably exact experiment in manuring requires the strict adherence to the methods which he describes. (*Journal Chem. Society, No. CCVLIII, p. 634.*)

Dr. A. B. Griffiths finds that in solutions containing an increased amount of ferrous sulphate up to .15 per cent. plants grow much better, especially those containing a large amount of chlorophyl; while in solutions containing .2 per cent., seeds will not germinate and plants die. (*Chem. News, vol. 50, p. 167.*) Other experiments of his tend to the conclusion that chlorophyl is a compound of iron with a glucoside. (*C. N., 49—237.*)

Dr. T. L. Phipson, about a year ago, published an article upon the production of oxygen by certain unicellular algæ. (*C. N., 48—205.*) He has since published the results of other experiments showing that plants have not the power to take carbon dioxide from water and decompose it liberating oxygen, if the water contains *only* carbon dioxide; something else is necessary, and this, he asserts, is hydrogen peroxide. He attributes the evolution of oxygen to reactions between CO_2 and $H_2\,O_2$ by which ternary compounds are formed in the plant and oxygen liberated. (*C. N., 50—37.*)

G. Bonnier and L. Mangin. Comparative experiments respecting the oxygen absorbed and the carbon dioxide evolved in the dark by various species of plants, show that the ratio between the two quantities is constant, whatever the temperature, but that the ratio varies for different plants. The activity of the action increases rapidly with the temperature. (*J. C. S., CCLXI—857.*)

Pichard has made some interesting researches in nitrification. He finds that certain salts, if applied to the soil exercise an energetic nitrifying power. The effect was especially marked with calcium sulphate. Taking that as 100, the nitrifying power of sodium sulphate was 47.91; of potassium sulphate, 35.78; of calcium carbonate, 13.32; and of magnesium carbonate, 12.52. This remarkable power of gypsum explains its beneficial action when used as a fertilizer. Its application to soils poor in calcium compounds cannot be too highly recommended. (*J. C. S., CCLXII—924.*)

G. Marek has made analyses determining the distribution of the sugar in the beet. He divided the beet into eight sections from top to bottom, and determined the sugar in each. The rotatory power was greatest in the second section, and decreased downward. The upper section is between the fifth and sixth in amount of sugar. He also determined the lateral distribution of the sugar, and found the largest amount in a zone between one-seventh and two-sevenths of the distance from the outside to the center. (*J. C. S., CCLX—766.*)

Messrs. Lawes and Gilbert have published a long memoir on the composition of the ash of wheat straw and wheat grain, showing the influence of varying seasons and different manures. The length of the paper forbids any attempt at abstraction. (*J. C. S., CCLXI—305.*)

The most striking feature in the progress of analytical chemistry, is the number of methods which have been proposed for the detection or estimation of nitrogen in its various combinations. Accurate valuations of nitrogenous fertilizers are of growing importance to agriculture, and the attention of agricultural chemists throughout the world is directed toward this subject. At the instance of the German Manure Manufacturers' Association, a general meeting of chemists was held at Wiesbaden, last May, under the Presidency of Prof. Fresenius, to consider proposals for uniform methods for nitrogen determinations. They agreed upon methods for the preparation of samples, and the determination of ammoniacal, organic, and nitric nitrogen. (*C. N., 50—180.*)

A new method of estimating organic nitrogen has been devised by J. Kjeldahl. The dried substance is digested for several hours with concentrated sulphuric acid, at near the boiling point of the acid. The conversion of the nitrogen into ammonia is completed by adding potassium permanganate in very small quantities until an excess is indicated by the solution becoming green. When cold the solution is made alkaline by a strong solution of caustic soda and the ammonia is distilled into standard acid. The author has obtained satisfactory results with a large variety of nitrogenous substances. (*J. C. S., CCLVI—364.*)

Prof. S. W. Johnson finds that simply calcium hydrate may be substituted for soda-lime in the conversion of organic nitrogen into ammonia for purposes of analysis. (*Am. Chem. Journal, Vol. 6, p. 60.*)

G. Lunge.—(1) Lime, soda and magnesia in excess liberate all the ammonia in ammonium chloride equally well. (2) Amines are liberated under the same circumstances as ammonia, so that the assumption that magnesia avoids the decomposition of amines which may be present in commercial manures is quite erroneous. (*J. C. S., CCLX—776.*)

A. G. Green and S. Rideal have published a method of determining nitrous acid by means of a one-tenth normal solution of pure aniline, which they maintain is more accurate than the permanganate process, and can be used in the presence of oxidizable substances. (*C. N., 49—173.*)

M. Arnaud has developed a method of precipitating nitric acid as cinchonamine nitrate. It may be used for the estimation of nitric acid in natural waters and in plants. The method possesses several advantages, among which is the high molecular weight of the precipitate. Very good results have been obtained, but the details of the process cannot be given here. (*C. N., 50—103.*)

Several qualitative tests for nitric acid and nitrous acids have been proposed, but space forbids any further mention of them.

Considerable attention has also been given to the determination of carbon in iron and steel. Most of the progress, however, consists in modifications of the well-known methods. Zaboudsky decomposes the finely pulverized sample by means of a mixture of sodium chloride and cupric chloride, instead of cupric-ammonium chloride. The decomposition is completed in about forty-five minutes. His method contains other modifications of the ordinary process also. (*C. N., 50—57.*)

A. B. Clemence filters the carbon after its separation from iron directly into a platinum combustion tube. The tube is eleven and one-half inches long, three-fourths of an inch wide for seven inches, and then contracts rapidly to three-sixteenths of an inch. An asbestos filter is placed at the point where the contraction begins. (*C. N., 48—206.*)

R. W. Atkinson has made some valuable investigations on the standarizing of potassium bichromate. He also condemns the use of stannous chloride as a reducing agent in analyses of iron, on account of the difficulty with which the excess of the reagent is accurately destroyed. Since zinc chloride diminishes the delicacy of the ferri-cyanide reaction, he strongly recommends ammonium bisulphite for the reduction of ferric compounds when potassium bichromate is used in the titration. (*C. N., 49—217.*

G. Bruel uses sodium salicylate as an indicator in the titration of ferric solutions with sodium thiosulphate. (*J. C. S., CCLVI—367.*)

Thomas Moore describes a method of separating nickel and zinc, which seems to be much superior to the method with hydrogen sulphide and sodium acetate. (*C. N.*, 501—51.)

Mr. E. R. Dryer finds brucine a more convenient, more delicate and more striking test for tin than the mercuric chloride test. .1 gram brucine is dissolved in 1 c.c. strong nitric acid and diluted to 50 c.c. (*C. N., 48—257.*)

A new method of separating strontium and calcium has been devised by M. D. Sidersky. It is based on the fact that when a mixture of ammonium sulphate and ammonium oxalate is added to a solution containing strontium and calcium, the strontium is precipitated as sulphate while the calcium remains in solution and may be precipitated from the filtrate by supersaturating with ammonia. The reagent contains three per cent. of ammonium oxalate and twenty per cent. of ammonium sulphate. (*C. N., 48 —296.*)

A. Cavazzi.—In a mixture of chlorides, bromides and iodides, the iodine may be determined by distilling the solution with ferric sulphate and collecting the iodine in potash. The ferric sulphate must be calcined to remove traces of acid, and a small amount of ferrous sulphate is added to increase the solubility of the ferric salt. *C. N., 49—14.*)

David Lindo has made an exhaustive examination of the oxalic acid method of separating phosphoric acid, for determination as magnesium pyro-phosphate. Space does not admit of useful abstraction. (*C. N., 48—217, 230 and 239; also 49—247.*)

Thomas S. Gladding, in a series of experiments on natural phosphates, artificial soils and natural soils, has demonstrated that soluble phosphates become reverted very rapidly in both natural and artificial soils, and that if iron or alumina is present the reverted phosphates are not entirely taken up by a neutral solution of ammonium citrate at 40° C., but are entirely dissolved by the same reagent at 65° C. (*Am. Chem. Jour., 6—1.*)

Prof. Lord recommends the use of ammonium fluoride, instead of a mixture of

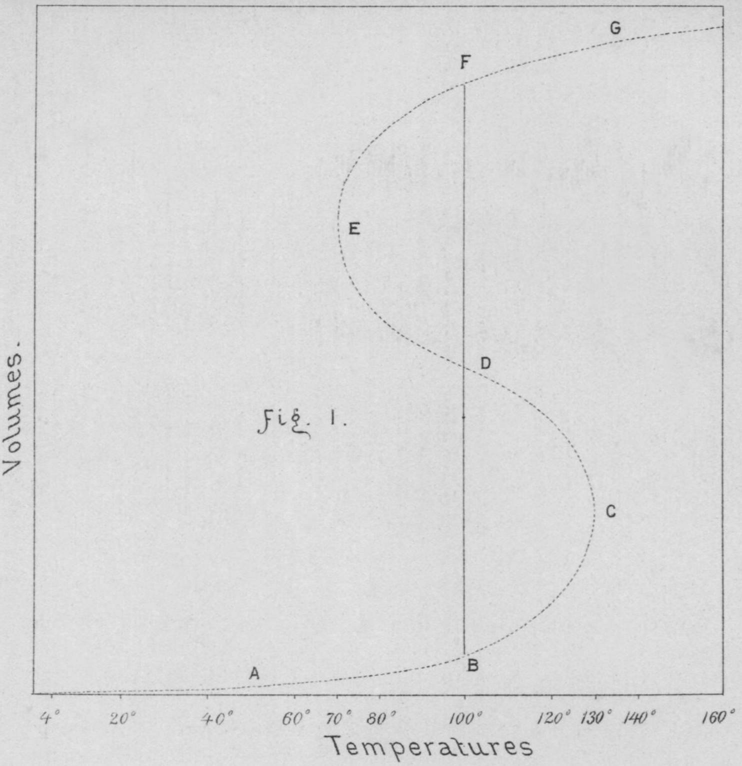

Fig. 1.

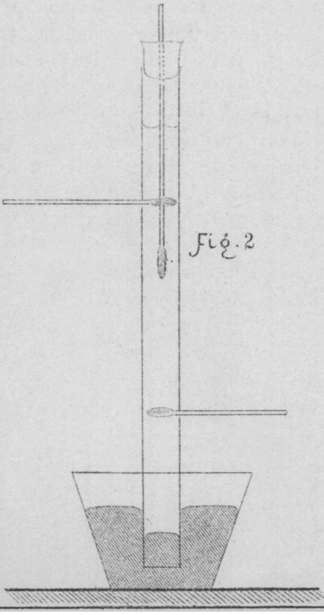

Fig. 2

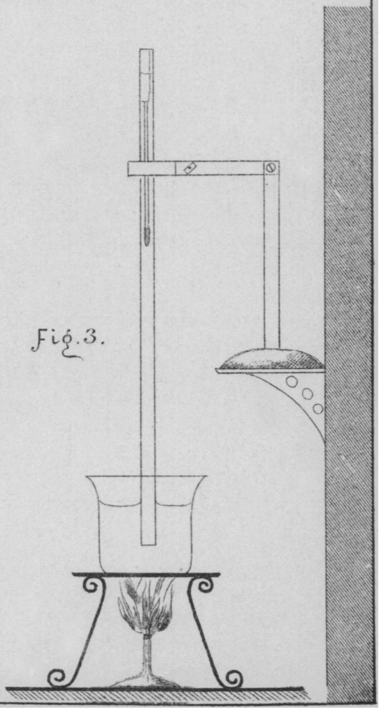

Fig. 3.

fluor-spar and potassium bisulphate, as a blow-pipe reagent in the detection of boron and the alkalies in their mineral combinations. (*C. N., 49—269.*)

According to E. Fischer, para-amido-dimethyl-aniline sulphate is a much more delicate test for hydrogen sulphide than either lead acetate or sodium nitro-prusside. (*J. C. S., CCIV—109.*)

For the detection of free sulphuric acid in vinegar, Wharton evaporates down to a syrup, lets cool to a hand-heat, and then stirs in a few centigrams of potassium chlorate. If there is more than one per cent. of sulphuric acid the mass ignites violently. Smaller quantities are detected by the odor of chlorine. (*C. N, 50—68.*)

R. T. Thompson has made a large number of observations on the use of litmus, rosolic acid, methyl-orange, phenacetolin, and phenolphthaleïn as indicators. The writer can only refer to the original articles. (*C. N., 49—32, 38 and 119.*)

EXPERIMENTS UPON SUPER-HEATED LIQUIDS AND UPON THE SUPER-SATURATION OF VAPORS.

EDWARD L. NICHOLS, PH. D.

I.

It is the purpose of this paper to describe some experiments upon the behavior of liquids heated beyond their boiling points under conditions which prevent ebullition, and of vapors cooled below the temperatures at which they ordinarily return to the liquid state.

Professor James Thomson*, in a discussion of Andrews's† well-known experiments on the continuity of the liquid and gaseous states, has shown that there are reasons for thinking that under proper conditions liquids might be converted into vapor even below the critical temperature without discontinuity; and he has shown the general form which the curve indicating the changes of volume might be expected to take. The change of state may be brought about by decrease of pressure or by increase of temperature. The former was the method adopted by Andrews in his research upon carbonic acid, and the curves given in Thomson's paper, based upon those experiments, are isothermal curves indicating variations of volume with the pressure. All that he has said on this subject is applicable, however, to methods in which the temperature is varied.

When heat is applied to a liquid at ordinary pressures, volume and temperature vary simultaneously until the boiling point is reached, when the temperature becomes constant and the familiar expansion-curve becomes a straight line, parallel to the axis along which volumes are measured. Figure 1 shows this curve (A B F G) in the case of water heated at a pressure of 760 mm. We know from the experiments of Donny‡, Dufour§ and others upon superheated liquids, that the curve does not always take this form, since water, holding no absorbed gases and contained in perfectly clean vessels, can be heated far above its boiling point without ebullition. The general form pointed out by Thomson for the isothermal method, but applied to the isobaric expansion-curve, is shown in the dotted line (B C D E F). The condition under which a liquid will follow the limb B C D is the absence of absorbed gases. The limb F E D should be obtained by cooling a vapor in the absence of its liquid.

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*James Thomson; Report of the British Association for the Advancement of Science, 1871; also Proceedings of the Royal Society, 1859 and 1871.

†Andrews; Philosophical Transactions, 1869.

‡Donny; Annales de Chimie, 1846, 3d series, Vol. XVI.

§Dufour; Bibliotheque Universelle, Archives 1861, Vol. XII.